JET-COOLED, CONFORMER-SPECIFIC IR SPECTRA OF CYCLICALLY-CONSTRAINED β-PEPTIDES. DOES CONDENSED PHASE STRUCTURE SURVIVE THE VACUUM?

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We present laser-desorbed, jet-cooled, conformation-specific UV and IR data on a series of increasingly complex β-peptide oligomers: Ac-(ACHC)$_2$-NHBn, Ac-ACHC-m$_4$ACHC-NHBn, Ac-m$_5$ACHC-m$_4$ACHC-NHBn, Ac-m$_4$ACHC-ACHC-NHBn, Ac-m$_4$ACHC-m$_5$ACHC-NHBn, Ac-(ACHC)$_3$-NHBn, and Ac-(ACHC)$_4$-NHBn. Synthetic foldamers are polymers composed of non-natural building blocks which either mimic, or expand upon, nature's preferred secondary structures which are accessible to pure α-amino acid sequences. The ring-constrained β-amino acid, *cis*-2-aminocyclohexanecarboxylic acid (ACHC), is one such non-natural building block which when polymerized with alternating chirality has been shown to adopt both right- and left-handed 12/10 mixed helices in solution and crystalline form. ACHC may adopt two local minima conformations: one in which the NH is axial (ax) with respect to the cyclohexane chair and the C=O is equatorial (eq), and vice versa. In poly-ACHC sequences, the cooperative conformational isomerization between these two minima switches the screw-sense of the 12/10 helix. The use of the more rigid β-amino acids, *cis*-2-amino-*cis*-4-methylcyclohexanecarboxylic acid (m$_4$ACHC) and *cis*-2-amino-*cis*-5-methylcyclohexanecarboxylic acid (m$_5$ACHC) sterically lock the ACHC residue into one of its two minima, depending on the stereochemical patterning at the ring's three stereocenters. The isolated, solvent-free conformational preferences will be compared with condensed phase data, and the energetic impact of the benzyl chromophore on preferred structure will be discussed.